Adaptive Analytic Mapping Procedures for Simple Accurate Calculation of Scattering Lengths and Photoassociation Absorption Intensities

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What is a 'scattering length', and Why do we care ?

- In the study of ultracold gases, the collisional properties of slow atomic collisions is a central concern.
- In the limit of zero kinetic energy, the collision cross-section for a gas of atoms of mass $m = 2\mu$ is $\sigma = 4\pi\, {a_s}^2$ where a_s is the S-wave scattering length.
- Scattering theory tells us that the scattering length is defined as

$$a_s = \left\{ \lim_{k \to 0} \frac{1}{k} \cot[\eta_s(k)] \right\}$$

where $\eta_s(k)$ is the S-wave scattering phase shift at collision wavenumber $k = \sqrt{2\mu\, E/\hbar^2}$ for collision energy E.

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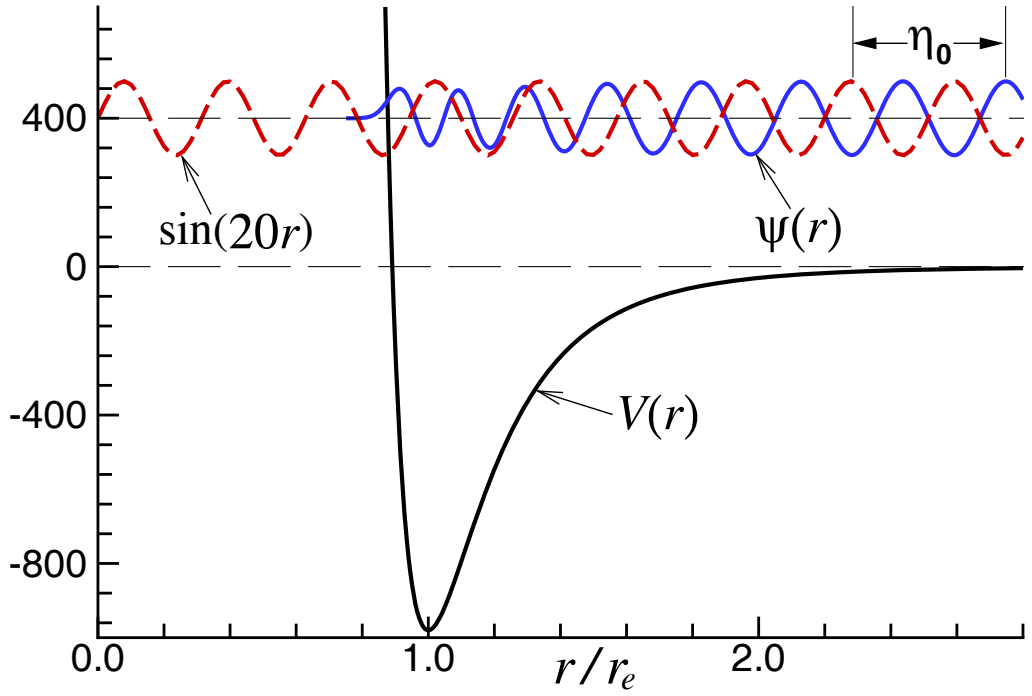
But what is a 'scattering phase shift' ?

Ans: *the asymptotic shift in phase (in radians) between the actual continuum wavefunction and the phase that wavefunction would have if* $V(r) = 0$.



Calculating a scattering length from phase shifts would (at best) be tedious, since:

- at every energy E we must propagate the wavefunction to *very large* r (to where the potential is negligible), before comparing it with the zero-potential solution to determine the phase difference
- this must be repeated at a sequence of ever-lower energies, and the result extrapolated to $E = 0$ (or $k = 0$) to obtain: $a_s = \left\{ \lim_{k \to 0} \frac{1}{k} \cot[\eta_s(k)] \right\}$

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A simpler definition of a 'scattering length' !

Theory also tells us that the asymptotic behaviour of the continuum wavefunction in the limit $E \to 0$ becomes $\psi(r) \simeq (r - a_s)$.

Question: *How can a wavefunction be linear ?*

Ans. The conventional radial Schrödinger equation is

$$\frac{d^2\psi(r)}{dr^2} = -Q(r)\,\psi(r) \qquad \text{in which} \qquad Q(r) = -\frac{2\mu}{\hbar^2}\,[E - V(r)]$$

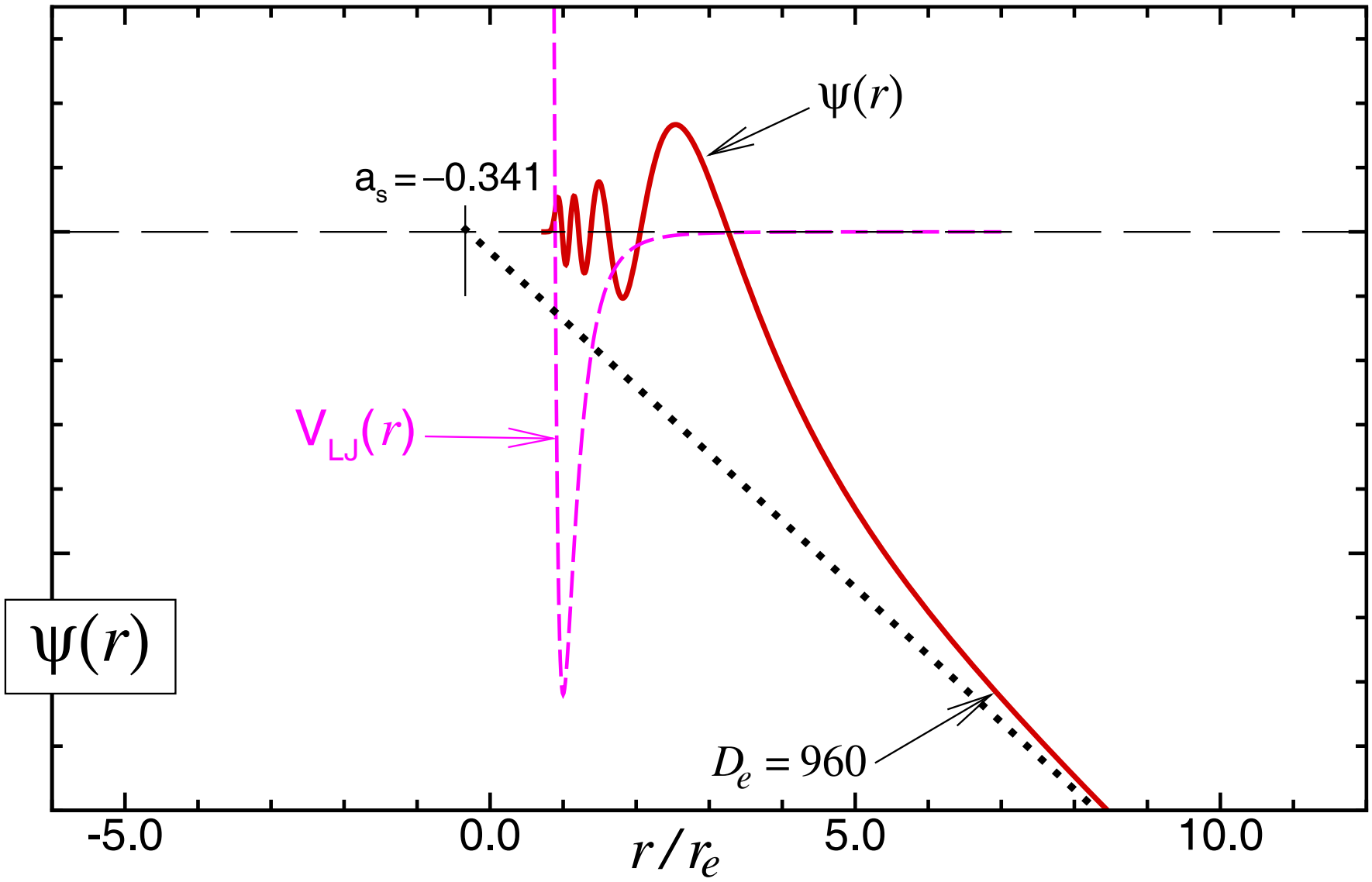
At the continuum threshold $E = V(r = \infty) = 0$

so at very large r this equation becomes simply: $\dfrac{d^2\psi(r)}{dr^2} = 0$

and its 'normalized' solution is $\psi(r) = (r - a_s)$

Consider the Schrödinger equation solution at $E = V(r = \infty) = 0$

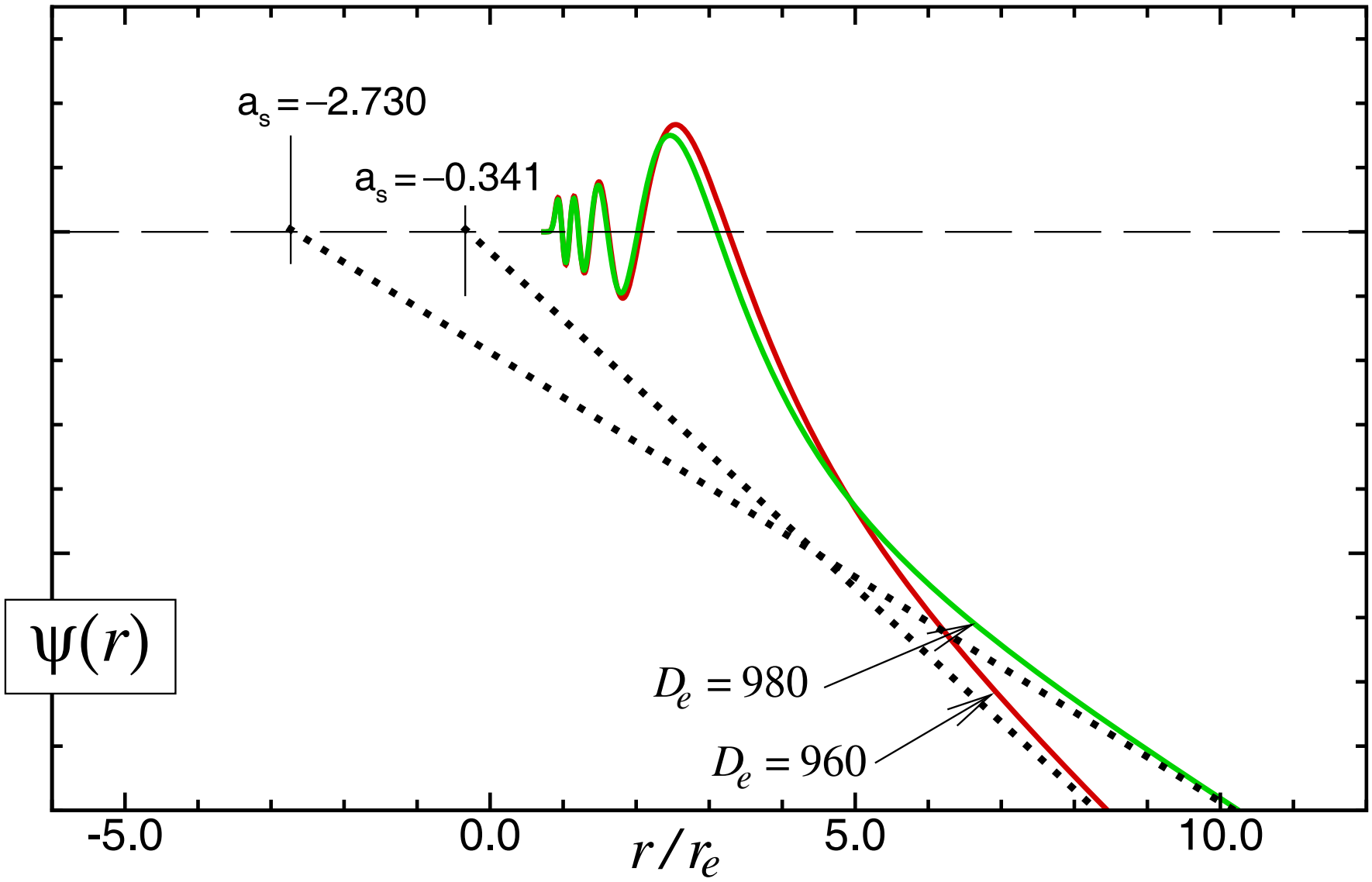
for an LJ(12,6) potential with depth $\mathfrak{D}_e = 960\ \mathrm{cm}^{-1}$ which supports 7 bound levels



Since asymptotically $\psi(r) \simeq (r - a)$, extrapolating back from the limiting long-range region gives a_s as the intercept. *Then on making the well deeper . . .*

Consider the Schrödinger equation solution at $E = V(r=\infty) = 0$

for LJ(12,6) potentials with depths $\mathfrak{D}_e = 960$ & $980\ \mathrm{cm}^{-1}$ ...



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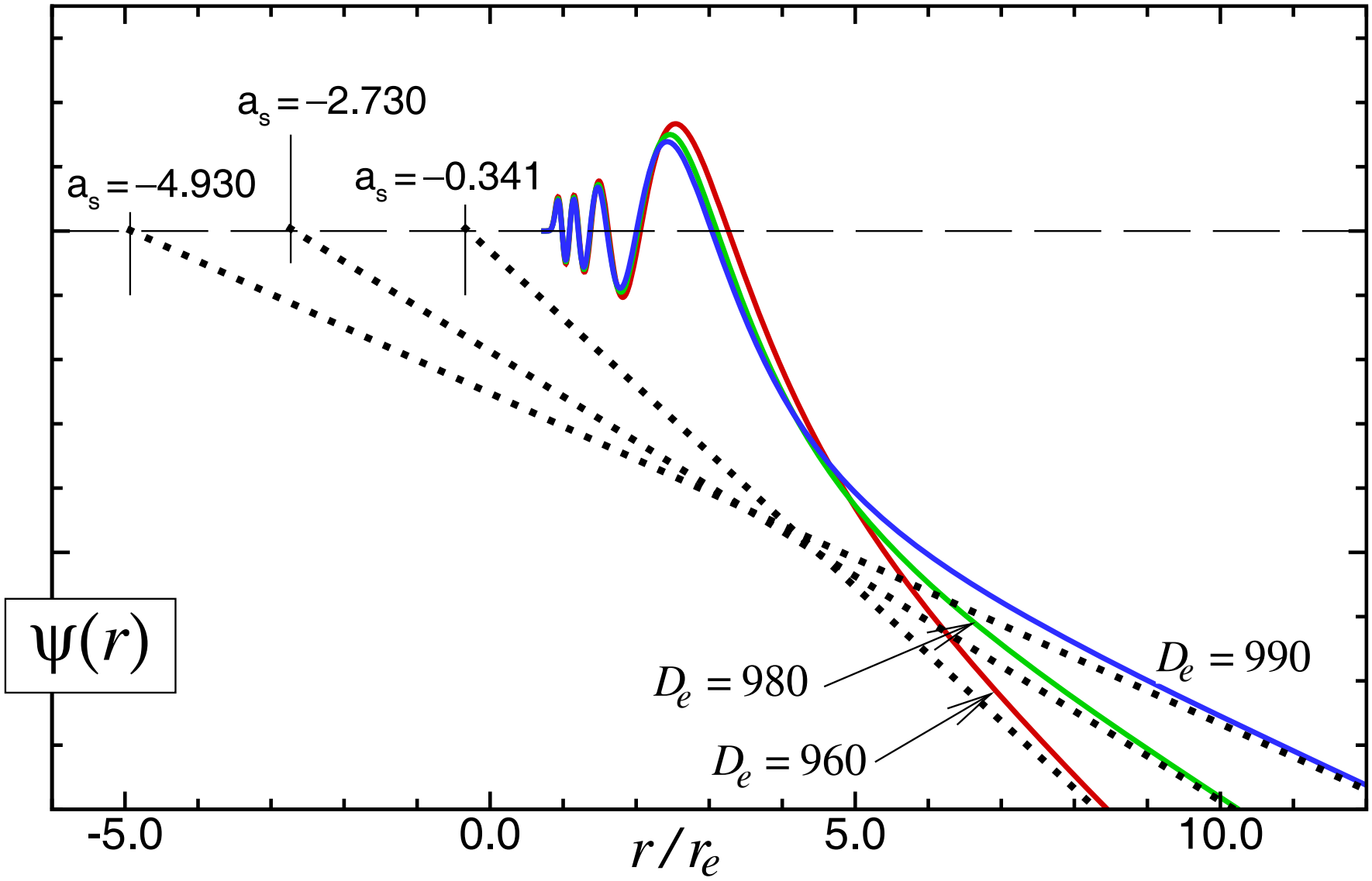
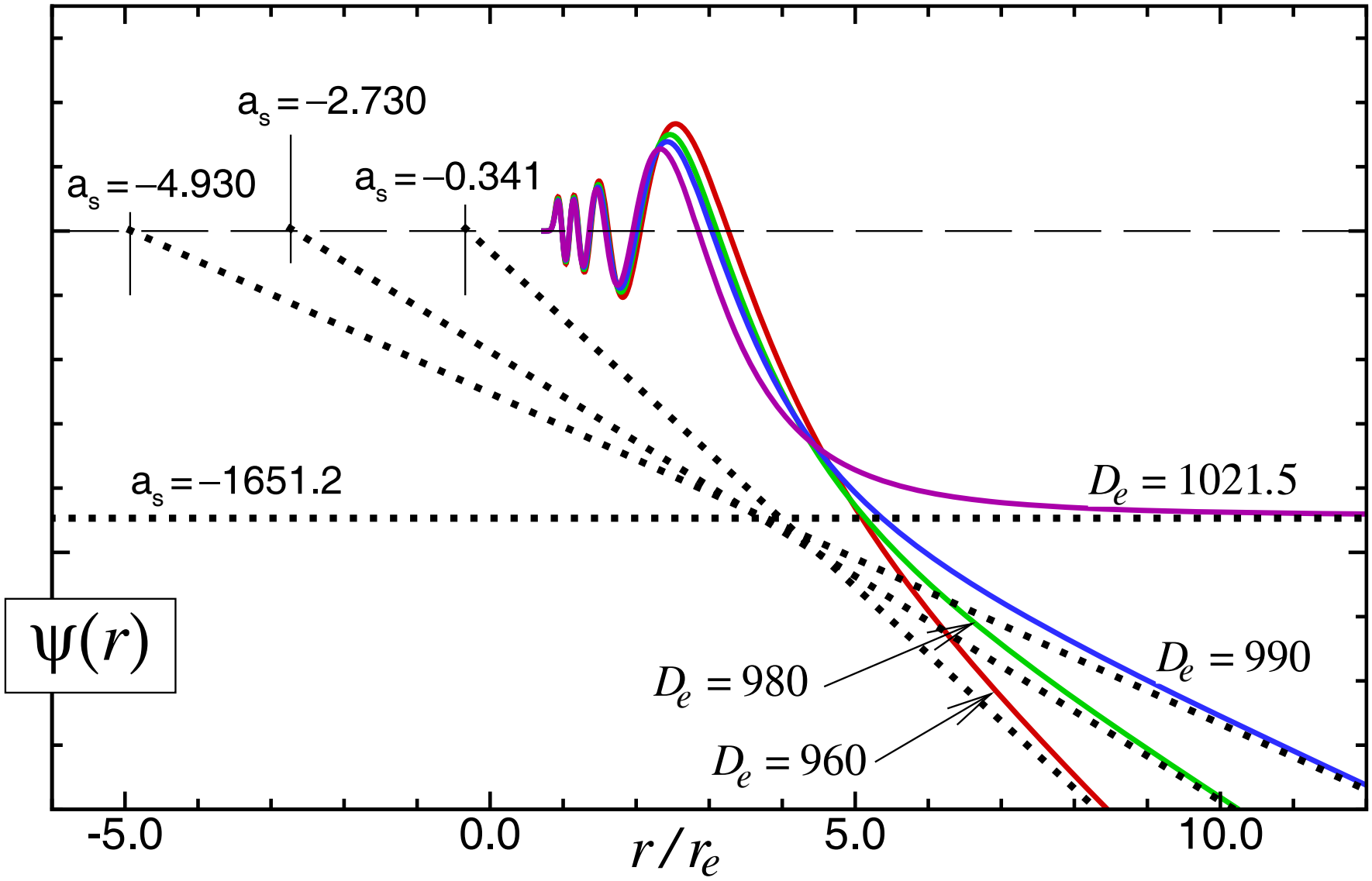


Consider the Schrödinger equation solution at $E = V(r=\infty) = 0$

for LJ(12,6) potentials with depth $\mathfrak{D}_e = 960\,,\ \ 980\,,\ \ 990\ \ \&\ \ 1021.5\ \mathrm{cm}^{-1}\ \ \ldots$



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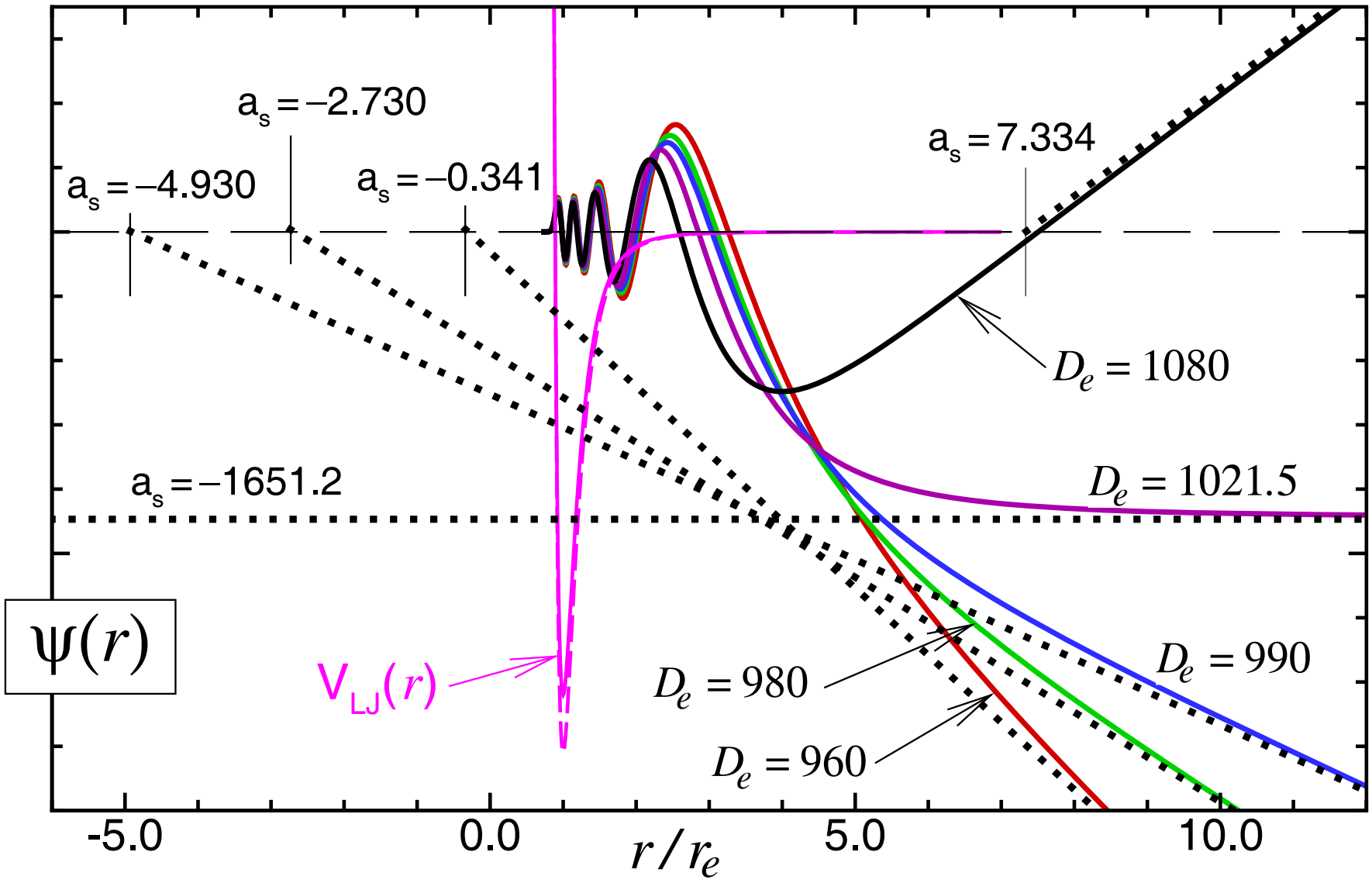


Thus, • calculate the $E=0$ wavefunction out to very large distance

• extrapolate linearly back to the intercept to get η_s

What is the Problem ?

When solving the radial Schrödinger equation at $E = V(r = \infty) = 0$:

- the wavefunctions extend across an infinite domain
- wavefunction amplitude and oscillation rate changes very dramatically across that domain !

As a result, when solving the radial Schrödinger equation at energy $E = V(r = \infty) = 0$

- No basis set method will work!
- Numerical integration with a mesh size suitable for small r will require extremely large radial arrays!
- This very large number of integration mesh points makes such calculations quite CPU intensive!
- Truncating the radial integration at some finite distance will introduce problems.

What is the Solution ?

Start from the conventional radial Schrödinger equation

$$\frac{d^2\psi(r)}{dr^2} = -\,Q(r)\,\psi(r) \qquad \text{in which} \qquad Q(r) = \frac{2\mu}{\hbar^2}\,[V(\infty) - V(r)]$$

If we now

- map the radial coordinate $r \in [0, \infty)$ onto a new radial variable with a finite domain: $y = y(r) \in [a, b]$
- and make the substitution $\psi(r) = \sqrt{g(y)}\;\phi(y)$ where $g(y) \equiv \dfrac{dr(y)}{dy}$
- our differential equation becomes

$$\frac{d^2\phi(y)}{dy^2} = -\,\widetilde{Q}(y)\,\phi(y) \qquad \text{in which} \qquad \widetilde{Q}(y) = -\,g(y)^2\,Q(r(y)) + F(y)$$

where both $g(y)$ and $F(y) \equiv \dfrac{g''}{2g} - \dfrac{3}{4}\left(\dfrac{g'}{g}\right)^2$ depend only on the definition of the variable mapping.

Our new differential equation in y can readily be solved using *exactly the same array of techniques* used for treating the conventional equation in r !

How do we define the variable mapping ?

Many possibilities, but two particularly convenient choices are

$$y(r) \;=\; \frac{r-\bar{r}}{r+\bar{r}} \qquad \textit{or} \qquad y(r) \;=\; \frac{2}{\pi}\,\arctan\left\{\,\alpha\left(\frac{r}{\bar{r}}-1\right)\right\}$$

where α is a positive real number and $\bar{r}$ a fixed reference distance.

With these choices the domain $[a,b]=[-1,\,+1]$ and

$$\left.\begin{array}{rcl} g(y) & \equiv & \frac{dr(y)}{dy} \;=\; \frac{2\bar{r}}{(1-y)^2} \\ F(y) & = & 0 \end{array}\right\} \qquad \textit{or} \qquad \left\{\begin{array}{rcl} g(y) & = & \frac{\pi\,\bar{r}}{2\,\alpha\,\cos^2(\pi\,y/2)} \\ F(y) & = & \pi^2/4 \end{array}\right.$$

After making this transformation, we can solve the radial Schrödinger equation on the entire interval $y\in[-1,\,+1]$ ($r\in[0,\,\infty]$) using any standard method !

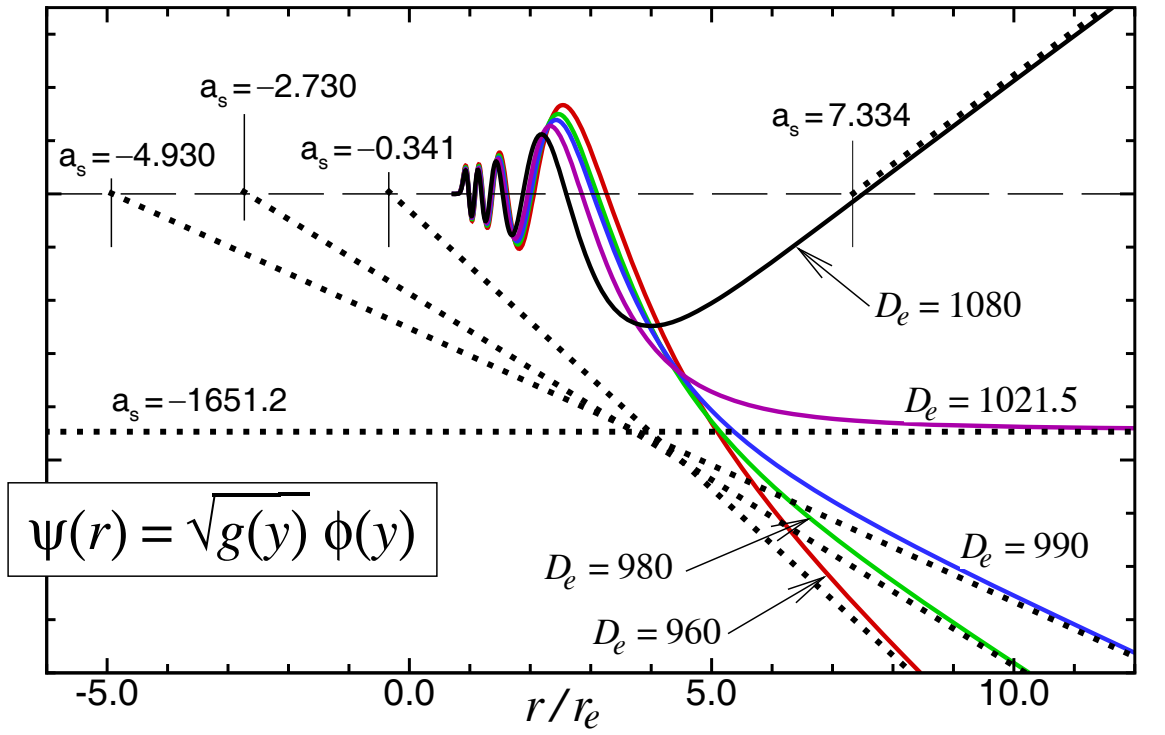
Then examination of the solution $\phi(y)$ at $y\approx 1$ allows us to either:

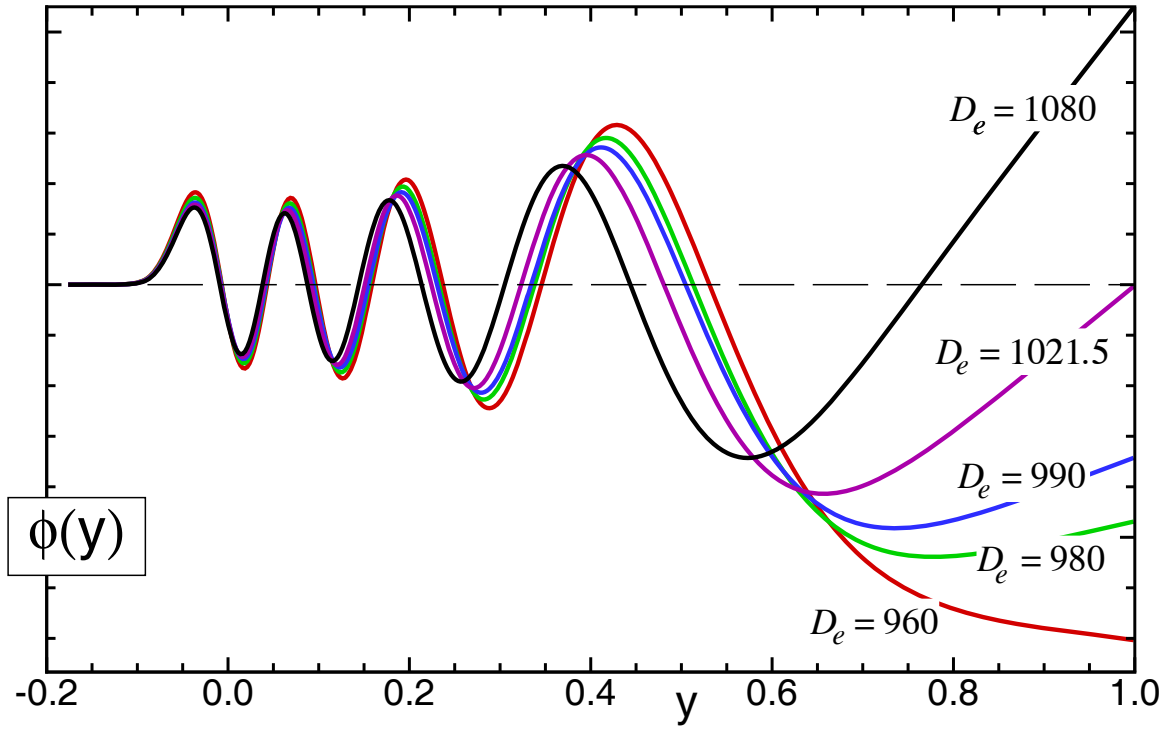
- convert $\phi(y_i)$ at two of the outermost mesh points to $\psi(r_i)=\sqrt{g(y)}\;\phi(y_i)$, and extrapolate $\psi(r)\simeq(r-a)$ back to determine the intercept of $r=a_s$ or
- use the log-derivative of $\phi(y_i)$ at $y=1$ to give

$$a_s \;=\; \bar{r}\left[1 \;+\; \frac{2}{\pi\,\alpha}\,\frac{d\,\ln\,\phi(y)}{dy}\right]_{y=1}$$

Compare the $E = 0$ solutions $\psi(r)$ and $\phi(y)$ for LJ(12,6) potentials with a range of well depths.

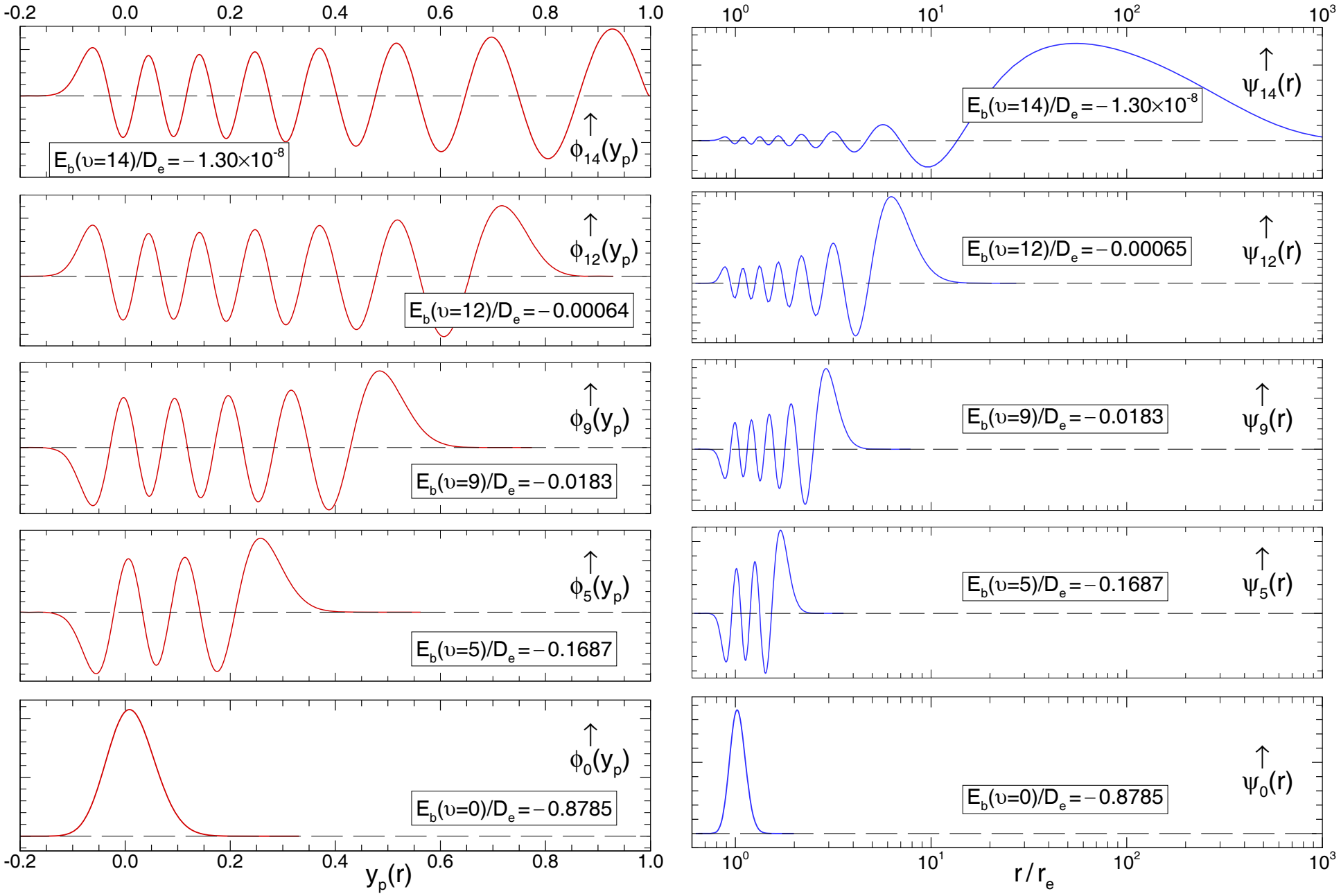
- Instead of having to integrate $\psi(r)$ out to *very* large distances,
- integrate $\phi(y)$ out to $y = 1$ and use its behaviour there to determine a_s .
- *This is a 'routine' type of calculation which can be performed using any standard bound-state code !*
- Easily achieve accuracy of $\gtrsim 9$ significant digits





The same transformation greatly simplifies calculations for bound states:

e.g., for a 15-level LJ(8,4) potential: [*see Phys.Rev.* **A 78**, *052510 (2008)*]



Hence . . . using this approach to solve the radial Schrödinger equation for bound states of one potential and at the asymptote of another allows routine calculation of photoassociation absorption intensities !

These capabilities will be incorporated in the next release of program **LEVEL**

[see `http://leroy.uwaterloo.ca/programs`]